Association of Metallurgical Engineers of Serbia *Review paper*
AMES *UDC:669.3:504.75.056,064:628.515=20*

POLLUTION PREVENTION AND CONTROL TECHNIQUES IN THE COPPER INDUSTRY

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ABSTRACT

In this paper, an approach is adopted to cover production of the copper from both primary and secondary raw materials. Process gasses are captured and cleaned in gas purification systems to reduce emission of dust and metal compounds. Uncaptured gases or fugitive emission are not treated. Careful plant design and process operations are needed to capture and treat process gasses where fugitive emission is significant. The use of suitable pre-treatment methods, furnace design, process management and process control are important factors to prevent environmental pollution.

Key words: copper, pollution, fugitive emission, gasses, dust.

INTRODUCTION

The main environmental issues for the primary copper production are the potential emission to air of dust and metals/metal compounds and of sulphur dioxide from roasting and smelting sulphide concentrates or using sulphur-containing fuels or other materials. The pyrometallurgical processes are potential sources of dust and metals from furnaces, reactors and the transfer of molten metal.

The main environmental issues for the secondary copper production are also related to the off-gases from the various furnaces and transfers that contain dust, metals and volatile organic components. There is also the potential for the formation of dioxins due to the presence of small amounts of chlorine in the secondary raw materials.

In summary the main issues for the production processes of copper comprise the following components:

- SO_2, dust, metal compounds, organic compounds, wastewater (metal compounds), residues such as furnace linings, sludge, filter dust and slag. Dioxin formation during treatment of secondary copper materials is also an issue.

APPLIED PROCESSES

Furnace design, the use of suitable pre-treatment methods and process control were identified as important features of best available techniques for pollution prevention and process control. The use of furnace sealing and enclosed transfers and storage is important in preventing fugitive emissions. The process choice is governed by the raw materials. The following Tables 1-3 summarize the furnaces used for the production of copper [1].

Table 1. Drying and roasting furnaces

Furnace	Material Used	Comment
Fluid bed dryer Flash dryer	Concentrates	Drying applications
Fluidised bed	Concentrates	Roasting
Rotary Kiln	Various scrap and residues	De-oiling Cu scrap

Table 2. Smelting and refining furnaces

Furnace	Material Used	Comment
Reverberatory	Concentrates, black copper	Smelting of Cu concentrates elsewhere in the world
Vanyucov	Concentrates	
Noranda	Concentrates	
El Teniente	Concentrates	
Baiyin	Concentrates	
Contop/Cyclone	Concentrates	
Outokumpu Flash Smelter	Concentrates	
Inco Flash Furnace	Concentrates	
Kivcet	Concentrates and secondary	
Mitsubishi process	Concentrates and anode	
ISA Smelt	Concentrates and secondary materials	
TBRC	Most secondary inc. slimes	
Mini Smelter	Scrap	
Submerged Electric Arc Furnace	Secondary materials	The open, semi closed and closed types are used
Rotary	Scrap and other secondary, blister copper	Oxidation and reaction with substrate
Peirce Smith	Matte and anode scrap	
Hoboken	Matte and anode scrap	
Outokumpu Flash Converter	Matte	
Noranda Converter	Matte	
Mitsubishi Converter	*Matte*	

Table 3. Melting furnaces

Furnace	Material Used	Comment
Induction	Clean metal and scrap	Induced stirring assists alloying. Vacuum can be applied for some metals
Contimelt	Copper anode, clean scrap and blister copper	Integrated furnace system
Shaft	Copper cathode, clean scrap	Reducing conditions
Drum (Thomas)	Copper scrap	Melting, fire refining

EMISSIONS TO AIR

Emissions to the environment depend on the collection or abatement systems that are used. The hierarchy of gas collection from all of the process stages is: process optimization and minimization of emissions, sealed reactors and furnaces and targeted fume collection.

The potential sources of emissions to air are summarised in the following Table 4, which also gives a review of prevention and treatment methods [1].

Table 4. Summary of sources and treatment/abatement options

Process stage	Component in off-gas	Treatment method
Materials handling and storage	Dust and metals	Correct storage, handling and transfer. Dust collection and fabric filter if necessary
Grinding, drying	Dust and metals	Process operation. Gas collection and fabric filter
Sintering/roasting Smelting Converting Fire refining	VOCs, dioxins	Afterburner, adsorbent or activated carbon addition
	Dust and metal compounds	Gas collection, gas cleaning in EP or fabric filter, heat recovery
	Carbon monoxide	Afterburner if necessary
	Sulphur dioxide	sulphuric acid plant (for sulphidic ores) or scrubber
Slag treatment	Dust and metals	Gas collection, cooling and fabric filter
	Sulphur dioxide	Scrubber
	Carbon monoxide	Afterburner
Thermal refining	Dust and metals.	Gas collection and fabric filter
	Sulphur dioxide.	Scrubber if necessary
Metal powder production	Dust and metals	Gas collection and fabric filter

Melting and casting	Dust and metals.	Gas collection and fabric filter.
	VOCs, dioxins (organic feed)	Afterburner (Carbon injection)
Note. Dust arrestment using a fabric filter may require the removal of hot particles to prevent fires. Hot electrostatic precipitators would be used in a gas cleaning system prior to a sulphuric acid plant or for wet gases.		

Sulphur capture is an important requirement when sulphidic ores or concentrates are roasted or smelted. The sulphur dioxide produced by the process is collected and can be recovered as sulphur, gypsum (if no cross-media effects) or sulphur dioxide or can be converted to sulphuric acid. The process choice depends on the existence of local markets for sulphur dioxide. The production of sulphuric acid in a double contact sulphuric acid plant with a minimum of four passes, or in a single contact plant with gypsum production from the tail gas and using a modern catalyst, are considered to be best available technique. Plant configuration will depend on the concentration of sulphur dioxide produced in the roasting or smelting stage.

Table 5. Emissions to air associated with the use of best available technique

Abatemet Technique	Associated Range	Comment
Fabric filter	Dust 1 - 5 mg/Nm^3 Metals – dependent on dust composition	Depends on characteristics of dust
Carbon or Bio filter	Total organic C < 20 mg/Nm^3	Phenol < 0.1 mg/Nm^3
Afterburner (including temperature quench for dioxin removal)	Total organic C < 5 - 15 mg/Nm^3 Dioxin < 0.1 - 0.5 ng/Nm^3 TEQ PAH (OSPAR 11) < 200 μgC/Nm^3 HCN < 2 mg/Nm^3	Designed for gas volume. Other techniques are available to reduce dioxins further by carbon/lime injection, catalytic reactors/filters
Optimized combustion conditions	Total organic C < 5 - 50 mg/Nm^3	
Wet EP Ceramic filter	Dust < 5 mg/Nm^3	Depends on characteristics e.g. dust, moisture or high temp.
Wet or semi-dry alkaline scrubber	SO_2 < 50 - 200 mg/Nm^3 Tar < 10 mg/Nm^3 Chlorine < 2 mg/Nm^3	
Alumina scrubber	Dust 1 - 5 mg/Nm^3 Hydrocarbon < 2 mg/Nm^3 PAH (OSPAR 11) < 200 μgC/Nm^3	
Sulphuric acid plant	> 99.7% conversion (double contact)	Including mercury scrubber using Boliden/Norzink process or thiosulphate scrubber Hg < 1 ppm in acid produced
	> 99.1% conversion (single contact)	
Cooler, EP, lime/carbon adsorption and fabric filter	PAH (OSPAR 11) < 200 μgC/Nm^3 Hydrocarbons (volatile) < 20 mgC/Nm^3 Hydrocarbons (condensed) < 2 mgC/Nm^3	

A summary of the emission levels associated with abatement systems that are considered to be best available techniques for the copper processes is shown in the following Table 5. Emissions to air are reported on the basis of collected emissions. Associated emissions are given as daily averages based on continuous monitoring during the operating period and standard conditions of 273 K, 101.3 kPa, measured oxygen content and dry gas without dilution of the gases with air. In cases where continuous monitoring is not practicable the value will be the average over the sampling period.

For the abatement system used, the characteristics of the gas and dust will be taken into account in the design of the system and the correct operating temperature used.

For some components, the variation in raw gas concentration during batch processes may affect the performance of the abatement system [1].

Process gases from primary and secondary copper production are captured and than cleaned in electrostatic precipitators and fabric filters and so the emissions of dust and metal compounds are reduced. Gas cleaning using wet scrubbers and wet electrostatic precipitators is particularly effective for process gases that undergo sulphur recovery in a sulphuric acid plant. Afterburners and carbon absorption are used to remove dioxins and VOCs. Uncaptured gases or fugitive emissions, however, are not treated.

Dust emissions also occur from storage, handling and the pre-treatment of raw materials where fugitive dust emissions also play an important role. This is true for both primary and secondary production, as their significance can be much greater than captured and abated emissions [2]. Careful plant design and process operations are needed to capture and treat process gases where fugitive emissions are significant. The following Table 6 shows that fugitive or uncaptured emissions are important issues [1].

Table 6. Comparison of abated and fugitive dust loads at a primary copper smelter

	Dust emission kg/a	
	Before additional secondary gas collection (1992)	After additional secondary gas collection (1996)
Anode production t/a	220000	325000
Fugitive emissions Total Smelter	66490	32200
Smelter roofline	56160	17020
Primary smelter stack emissions. Smelter/acid plant	7990	7600
Stack-secondary hoods	2547	2116

For primary copper the reverberatory furnace is not considered to be best available technique. The other major influences are the blending of the raw materials, process control, management and the collection of fume.

PROCESS RESIDUES

Process residues are produced at various stages of the process and are highly dependent on the constituents of the raw materials [2]:

- filter dusts (using fabric filters or EPs or using scrubbers or wet EPs) can be recycled within the same plant or used for the recovery of other metals; dust and sweepings from raw materials handling - feed for the main process;
- slag from smelting, converting, refining and melting furnaces - construction material after slag treatment or recycle to smelter, return to process after treatment, metal recovery, recovery of salt and other material;
- electrolyte bleed, anode remnants and anode slime from electro-refining - return to converter or recovery of precious metals;
- catalyst, acid sludge, weak acid from sulphuric acid plan – regeneration, safe disposal, leaching or disposal, respectivelly;
- refractory from furnace linings - use as slagging agent or disposal.

CONCLUSION

In copper industry like as other non-ferrous metals production, furnace design, the use of suitable pre-treatment methods and process control were identified as important features of best available technique.

The use of raw material blending to optimize the process prevents inappropriate material being used and maximizes process efficiency. Sampling and analysis of feed materials and the segregation of some materials are important factors in this technique.

Good design, maintenance and monitoring are important for all process and abatement stages. Sampling and monitoring of emissions to the environment should be carried out according to national or international standard methods. Important parameters that can be used for the control of process or abatement should be monitored. Continuous monitoring of key parameters should be carried out if practical.

REFERENCES

[1] Reference Document on Best Available Techniques in the Non-Ferrous Metals Industries, BAT Reference Document (BREF), European IPPC Bureau, Seville, Spain, 2001

[2] S. C. Bhatia, Industrial Pollution and Control / Pollution control in copper industry in Vol. II, New Delhi, CBS, 2002, 2 Vols., 1184 p., ISBN 81-239-0805-9 (Vol. I), 81-239-0806-7 (Vol. II)